

Emissions of Toxic Pollutants from Compressed Natural Gas (CNG) and Low Sulfur Diesel-Fueled Heavy-Duty Transit Buses Tested Over Multiple Driving Cycles

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Abstract

The number of heavy-duty vehicles using alternative fuels such as compressed natural gas (CNG) and new low-sulfur diesel fuel formulations and equipped with after-treatment devices are projected to increase. However, few peer-reviewed studies have characterized the emissions of particulate matter (PM) and other toxic compounds from these vehicles. In this study, chemical and biological analyses were used to characterize the identifiable toxic air pollutants emitted from both CNG and low-sulfur-diesel-fueled heavy-duty transit buses tested on a chassis dynamometer over three transient driving cycles and a steady-state cruise condition. The CNG bus had no after-treatment and the diesel bus was tested first equipped with an oxidation catalyst (OC) and then with a catalyzed diesel particulate filter (DPF). Emissions were analyzed for PM, volatile organic compounds (VOCs; determined on-site), polycyclic aromatic hydrocarbons (PAHs), and mutagenic activity. The 2000 model year CNG-fueled vehicle had the highest emissions of 1,3-Butadiene, benzene, and carbonyls (e.g., formaldehyde) of the three vehicle configurations tested in this study. The 1998 model year diesel bus equipped with an OC and fueled with low-sulfur diesel had the highest emission rates of PM and PAHs. The highest specific mutagenic activities (revertants/ μg PM, or potency) and the highest mutagen emission rates (revertants/mi) were from the CNG bus in strain TA98 tested over the New York Bus (NYB) driving cycle. The 1998 model year diesel bus with DPF had the lowest VOCs, PAH, and mutagenic activity emission. In general, the NYB driving cycle had the highest emission rates (g/mi) and the Urban Dynamometer Driving Schedule (UDDS) had the lowest emission rates for all toxics tested over the three transient test cycles investigated. Also, transient emissions were in general, higher than steady state emissions. The emissions of toxic compounds from an in-use CNG transit bus (without an oxidation catalyst) and from a vehicle fueled with low-sulfur diesel fuel (equipped with DPF) were lower than from the low-sulfur diesel fueled vehicle equipped with OC. All vehicle configurations had generally lower emissions of toxics than an uncontrolled diesel engine. Tunnel backgrounds

(measurements without the vehicle running) were measured throughout this study and were helpful in determining the incremental increase in pollutant emissions. Also, the on-site determination of VOCs, especially 1,3-Butadiene helped minimize measurement losses due to sample degradation after collection.

Introduction

Diesel exhaust and diesel particulate matter is associated with lung cancer and non-cancer adverse respiratory health effects (1). Particulate matter (PM) from diesel engines is listed as a toxic air contaminant under the California Toxic Air Contaminants Program (1) and as an integral part of this Program, there is evaluation and implementation of control strategies (2). Approaches for reducing PM emitted from conventional diesel engines include the use of low sulfur diesel fuels with oxidation catalysts and/or particle traps. Another approach is to use an increasingly common alternative fuel such as compressed natural gas (CNG) for transit bus fleets (3). The effect of these approaches on the amount, number, density, or specific chemical composition of the PM emitted from in-use diesel engines has not been fully evaluated. There have been very few studies reporting on the gas-phase and semi-volatile toxic compounds emitted. With respect to PM, nanoparticles with lower mass and greater total surface area than fine particles (PM_{2.5}) may be present. The alteration and the formation of toxic compounds and potential changes in emissions toxicity when using after-treatment technologies are also unknown.

With respect to the toxic compounds emitted from diesel fuel formulations, investigators (4, 5) reported on a low sulfur diesel fuel (LSDF) and a reference diesel fuel (RDF) tested in a D12A 420 engine. The 1,3-Butadiene emissions were reported as relatively close to the detection limit (<10 mg/km). The authors reported that there were approximately 8.5 times more PM-associated PAHs and 4.5 times more semi-volatile PAHs emitted from the combustion of RDF than from LSDF.

Grägg (6) reported chassis dynamometer testing of a CNG fueled bus equipped with 9.6 L engine (Volvo) and oxidation catalyst (Engelhard Inc). The author reported that pyrene (36 to 150 $\mu\text{g}/\text{km}$) was the major semi-volatile PAH. The author also found lower PAH emissions from vehicles equipped with catalytic muffler and CRTTM than a vehicle equipped with ordinary muffler (7). Recently, a multi-institutional research effort was completed investigating ultra-low sulfur diesel fuels and DPFs in a number of trucks and buses (8). The investigators found considerable decreases in emissions for these new diesel fuels with controls. Chemical analyses of toxic compounds, including PAHs and mutagenicity were also reported (9, 10).

Very little has been published regarding the mutagenic activity of in-use vehicle engine emissions using either CNG or new diesel fuels, or from vehicles equipped with emission control devices. Grägg (6) reported that the mutagenic emissions from a CNG bus equipped with an oxidation catalyst were present in the single PM sample collected and semi-volatile samples. The highest emission rate was reported for the semi-volatile phase in TA 98 (+S9) while relatively low emissions were reported for the PM phase. Further, Grägg (6) qualitatively noted that there was measurable mutagenic activity for diesel vehicles equipped with CRTTM or oxidation catalyst, but the data was highly variable and was not reported.

Westerholm et al. (4) reported that emissions from a vehicle fueled with a reference fuel, compared with the low sulfur fuel, had 8-10 times more mutagenic activity in the PM phase and 2-3 times higher mutagenic activity in the vapor-phase emissions. A pilot study of liquefied natural gas (LNG) derived PM was positive for mutagenic activity (10). Very few studies have been published on CNG-fueled and DPF-equipped diesel emissions of toxic volatile organic compounds (VOCs) such as benzene and formaldehyde, especially over a series of established driving cycles. Grägg (6) reported that the formaldehyde and acetaldehyde emissions from a CNG bus (equipped with oxidation catalyst) ranged from 6.7 to 23 mg/mi for formaldehyde and was approximately 5 mg/mi for

acetaldehyde. Lev-On et al (9) reported that the highest levels of benzene were in transit buses without DPF or in CNG-fueled vehicles.

We report here on a study of PM, toxic pollutants, and mutagenicity emitted from two in-use “clean technology” transit buses: one fueled with CNG and one fueled with ultra-low sulfur diesel (ECD-1) equipped with either an oxidation catalyst or a Continuously Regenerating Trap (CRT™) (with muffler removed). These vehicles were tested using both transient and steady-state driving cycles. Furthermore, we acknowledge that relative to older buses or buses without aftertreatment, the emissions from our test vehicles will likely compare favorably. This comparison was not included as our focus here is current, in-use configurations.

Materials and Methods

Testing Facility

Testing was conducted at the California Air Resources Board Heavy Duty Emissions Testing Laboratory (HDETL) located at the Los Angeles County Metropolitan Transit Authority (LACMTA) Regional Rebuild Center near downtown Los Angeles as described previously (11). Briefly, the test vehicle was placed on a chassis dynamometer (Schenck-Pegasus) with a range of simulated inertial weights from 5,000 to 100,000 lbs, capable of absorbing up to 660 hp. Vehicle exhaust was diluted in a Horiba critical flow venturi, constant volume sample (CFV-CVS) primary 18-in diameter dilution tunnel that was operated at 2,500 scfm. Standard gaseous pollutants and particulate emission samples were collected as specified in the Code of Federal Regulations (40 CFR, Part 86, Subpart N). Primary dilution air for the tunnel was passed through HEPA filters and a bed of charcoal before entering the tunnel. The total PM samples for mass emission measurements were collected under double-dilution conditions from a 5-in diameter secondary dilution tunnel with pre-filtered dilution air (air passed through a HEPA filter capsule-cartridge).

Vehicle Configuration

Two buses were tested in three configurations as described in Table 1 and as previously described (11). Briefly, these configurations included: 1) a CNG 40-passenger New Flyer bus equipped with a 2000 DDC Series 50G engine (CNG.1 and CNG.2), 2) a diesel 40-passenger New Flyer bus equipped with a 1998 DDC Series 50 engine and a Nelson Exhaust System catalyzed muffler (ECD.OC), and 3) the same New Flyer diesel bus retrofitted with a Johnson Matthey Continuously Regenerating Trap (CRT™) in place of the muffler (ECD.CR). The CRT™ was installed new and allowed to run on the bus for approximately 2,000 miles prior to testing. The CNG bus had no after-treatment system, which is representative of the vast majority of the current LACMTA CNG bus fleet (3). The physical and chemical characteristics of the CNG and diesel fuels are summarized in Tables 2 and 3, respectively.

Table 1. Vehicle and engine specifications.

Characteristic	Vehicle Configuration		
	CNG.1/CNG.2	Diesel with Oxy Cat	Diesel with CRT™
Vehicle	New Flyer Transit	New Flyer Transit	New Flyer Transit
Engine Manufacturer	Detroit Diesel	Detroit Diesel	Detroit Diesel
Model	Series 50G	Series 50	Series 50
Model Year	2000	1998	1998
Displacement	8.5 L 4-Stroke	8.5 L 4-Stroke	8.5 L 4-Stroke
No. Cylinders	4	4	4
Vehicle Wt (lbs)	33,150	30,510	30,510
Fuel	Compressed Natural Gas	ECD-1 ^a Low sulfur	ECD-1 ^a Low sulfur
After-treatment	None	Catalyzed muffler	Continuously Regenerating Trap (CRT)

^a Emission Control Diesel Fuel

Table 2. Compressed Natural Gas (CNG) fuel^a characteristics.

Characteristic	CNG.1 Test ^b	CNG.2 Test ^c
	Mean ± SD	Mean
Methane (mole %)	94.33 ± 1.54	86.93
Ethane (mole %)	2.43 ± 0.84	6.4
C ₃ /Propane (mole %)	0.83 ± 0.55	3.6
CO ₂ +N ₂ (mole %)	2.14 ± 0.08	2.39
Oxygen (mole %)	0.07 ± 0.09	0.12
Sulfur (ppmv)	2.3 ± 1.69	1.3
Gross Heating Value (BTU/cf)	1031 ± 1457	1106

^aFuel obtained from MTA commercial supplier.

^bMean and SD from four (4) determinations.

^cSingle determination. California Fuel Specifications for methane: 88.0% min; for ethane: 6.0% max, and for propane: 3.0% max.

Table 3. Low sulfur diesel fuel (ECD-1) characteristics.

Property	Sample 1	Sample 2
Aromatics (v %)	20.9	20.9
Aromatics (wt%)	21.4	21.4
Sulfur, ppm	11	11
PNA ^a (wt%)	2.78	2.76
T10, °C	199	199
T50, °C	249	248
T90, °C	317	316
Density, g/mL	0.8285	0.8284

Fuel supplied by BP-ARCO.

^a Polynuclear Aromatics

Vehicle Test Cycles

Transient driving or test cycles included in this study were the Urban Dynamometer Driving Schedule (UDDS), the New York City Bus (NYB), and the Central Business District (CBD) cycles as previously described (11, and CFR 40, Subpart N). The Steady-State (SS) 55 mph cruise was 20-min in duration for the “baseline” diesel ECD.OC and 40-min for both CNG.1 and CNG.2 and for ECD.CR. Dynamometer test sequences were composed of multiple equivalent cycles to ensure collection of sufficient sample for analyses. For the SS runs, the chassis dynamometer applied road load and additional vehicle-specific load corresponding to approximately 60% of the available engine power, a condition determined experimentally.

Temporally, the CNG bus was tested first (CNG.1), followed by the diesel baseline (ECD.OC) and the CRT TM -equipped (ECD.CR) configurations. The CNG bus was re-tested (CNG.2) after approximately 3 months of normal service. Prior to the re-test, the O₂ sensor module was replaced on the CNG vehicle and the engine software was upgraded during regularly scheduled maintenance (11).

Emissions Sampling

Prior to sampling each day, a conditioning protocol for the system was performed by first running dilution air through the dilution tunnel for 60 min (1.5×10^5 ft³ of dilution air). Immediately preceding the initiation of the test cycles, the engine was run at idle for a minimum of 15 min, followed

by a steady state (55 mph) warm up run of 20 min. Emissions of THC, NO_x, and CO were determined as prescribed in the CFR using flame ionization detection, chemiluminescence, and non-dispersive infrared detection, respectively, as previously reported (13).

Filters used for PAH and bioassay analyses were 70 mm Teflon-coated glass fiber filters (T60A20, Pall-Gelman, Ann Arbor, MI) that were pre-cleaned in both methanol (3 times) followed by dichloromethane (3 times). Polyurethane foam (PUF) media were pre-cleaned by sonication in hexane (3 times) and in acetone (3 times). Filters were pre-weighed in a temperature and humidity controlled room as per the CFR. The XAD-4 resin (pre-washed; Altech Associates, Inc., Deerfield, IL) was cleaned by sonication in methanol (3 times) and in dichloromethane (3 times).

Samples for PAH analyses were collected from the secondary dilution tunnel with a sampling train (flow rate ~ 3.5 scfm) that consisted of pre-cleaned filters (two 70 mm T60A20 filters placed in series), PUF, and XAD-4. Samples for the bioassay were taken from the primary dilution tunnel adjacent to the inlet of the secondary dilution tunnel for PM emissions. Regulated gaseous emissions were also sampled from this location. Samples for the bioassay were collected at a nominal flow rate of 3 cfm over multiple cycles for each vehicle configuration. Depending on the test cycle, filters were changed after each set of 2 or 3 test cycles, while adsorbents were changed after completing the test cycle series (usually 4 to 6 cycles).

Tunnel background (system blank) samples were obtained daily for each driving cycle type to determine sampling system contribution to the toxic pollutants measured. We felt that tunnel backgrounds needed to be measured for the current study of relatively lower emission-type heavy-duty vehicles. To our knowledge, this was the one of the first extensive emission studies incorporating these comprehensive background measurements into the experimental design. This background consisted of collecting samples in identical fashion to the corresponding driving cycle sample, except that the engine was not running. Also, for collecting tunnel background samples, the exhaust transfer line was disconnected from the dilution tunnel and the remaining exhaust inlet port to the tunnel was capped.

All regulated pollutants and toxic compounds were collected in parallel during the tunnel background sample collection.

After each test, filters were placed in a temperature and humidity controlled room, were allowed to equilibrate between 4 and 10 hrs, and were re-weighed. The filters were packaged in glassine paper, wrapped in foil and stored at -20°C . The PUF and XAD in the Teflon sampling holder were capped, wrapped in foil and shipped to the laboratory in blue ice. Upon arrival, the PUF and XAD were separated and stored in pre-cleaned amber glass bottles (Teflon-lined cap) and stored at -20°C . All media were covered with foil or handled under subdued light to minimize photooxidation.

Chemicals

Internal standard solution containing 16 deuterated-PAHs was obtained from Cambridge Isotope Laboratories Inc. (Andover, MA). Standard Reference Material SRM 2260, and native PAHs in toluene (nominal 60 ng/uL), were obtained from the National Institute of Standards and Technology (NIST; Gaithersburg, MD). Biphenyl- d_{10} and p-terphenyl- d_{14} were obtained from Restek (Bellefonte, PA). Benzo(a)pyrene, 2-nitrofluorene, and dimethylsulfoxide (DMSO, HPLC-grade) were obtained from Aldrich Chemical Co. (Milwaukee, WI). The solvents dichloromethane (DCM) [Spectro-Grade; EM Sciences (Darmstadt, Germany)], methanol (HPLC grade; Fisher Scientific), hexane, and acetone were obtained from Burdick and Jackson (Muskegon, MI).

PAH Analyses

Internal deuterated standards were added to the filters before extraction and the filters were extracted with DCM three times using sonication for 15 min each time period as previously described (14). The temperature of the sonication bath was maintained between 25°C and 30°C . Internal deuterated standards were added to the filters, the filters were extracted, and the extract was filtered through a $0.45\ \mu\text{m}$ filter (Acrodisc CR, Gelman Sciences, Ann Arbor, MI) and concentrated to 1 mL with nitrogen gas. Selected filter extracts were either further concentrated or pooled with other filter

extracts and further concentrated to a final volume of 50 or 100 μ L prior to analyses. The PUF samples were extracted with acetone as previously described (15). XAD samples were transferred to pre-cleaned separatory funnels and extracted with DCM four times. The XAD extracts were filtered and concentrated to 1 mL using the same procedure described for the filter extracts.

The PAH present on the Filter, PUF, and XAD were analyzed by gas chromatography/mass spectrometry (GC/MS) using a Hewlett-Packard (HP) Model 5890 Series II Gas Chromatograph interfaced to a HP 5972 mass selective detector (MSD). The injector was run in splitless mode and an electronic pressure controller was programmed for vacuum compensation and constant flow. The GC was equipped with a DB-5ms fused silica capillary column (30 m x 0.25 mm ID and 0.25 μ m film thickness; J and W Scientific, Inc., Folsom, CA). The MSD was run in selective ion monitoring (SIM) mode.

VOC Analyses

Toxic hydrocarbons in the diluted exhaust samples were analyzed on-site during sampling, which is unique for this type of analyses and incorporated using two GCs equipped with flame ionization detectors (GC-FID). This on-site analyses was particularly important for 1,3-Butadiene due to its rapid decay. Analytical determination followed Methods 1002 (for C₂-C₆ hydrocarbons) and 1003 (for C₆-C₁₂ hydrocarbons) of the California Air Resources Board (16). The GCs (Varian model 3400) were modified (Lotus Consulting Inc.) with specialized sampling valves and cryogenic trapping to improve sample recovery and chromatography. Mass emission rates from gas-phase concentrations in the diluted exhaust were calculated following the previously outlined procedures in the California Non-Methane Organic Gas Test Procedures (ARB, CNMOGTP, 1999). The target compounds included 1,3-butadiene, BTEX (benzene, toluene, ethylbenzene, and xylenes), styrene, and total non-methane hydrocarbons (NMHC). The 1,3-butadiene was measured using Method 1002 while the aromatics (BTEX and styrene) were measured using Method 1003.

Carbonyl sampling from the CVS-diluted exhaust were collected through a heated sample line (312°F) at a flow rate of ~1 L/min using two dinitrophenylhydrazine (DNPH) coated silica gel cartridges (Waters Associates, Wilford, MA) connected in series. The cartridges were later extracted and analyzed according to ARB Method 1004 of CNMOGTP using high performance liquid chromatography (HPLC) with UV detection. This method separates and quantifies 13 target compounds that represent the carbonyl species found in highest concentrations in gasoline vehicle exhaust, but do not represent a complete list of carbonyl compounds in the exhaust of diesel-powered vehicles.

Bioassay Analyses

The bioassay was conducted as previously reported (17, 18) and is a microsuspension procedure that increases the sensitivity over the plate incorporation procedure of Ames et al. (19). The PM extract was re-dissolved in DMSO and added directly to the assay. The PUF extract (in acetone) was solvent exchanged into DMSO under a gentle stream of nitrogen. Tester strains TA98 and TA100 were used with or without the incorporation of microsomal enzymes (+ or - S9). These tester strains are typically used for determining the genotoxic (DNA damaging) effects of PM samples from vehicular emissions, ambient air, and environmental samples. Strain TA98NR was also used to investigate the presence of nitro-PAHs (NPAHs) for selected sample extracts. This strain is insensitive to NPAHs and decreases in mutagenic activity imply the presence of these compounds (20).

The linear portion of the dose-response curve (line of best fit) was used to calculate the specific mutagenic activity (SMA; revertants per PM mass or per volume of extract for PM or vapor phase, respectively) from each vehicle configuration and background test. All doses of samples were tested in duplicate and the control values were determined in triplicate. The emissions of mutagenic activity (ME) were calculated from the total PM or vapor emitted per test.

RESULTS

PM Emissions

Regulated emissions were previously reported by our group (11) and the PM emissions are summarized in Table 4. The ultrafine PM emissions were discussed elsewhere (21). The PM emissions from the ECD.OC were the highest of all vehicle configurations and test cycles. For example, the highest PM (631 mg/mi) emission for the ECD.OC was observed for the NYB cycle, but during the SS test, the PM emission rate was similar to CNG.1. The CNG vehicle produced similar PM emission rates when tested over all transient cycles during the CNG.1 and CNG.2 test periods (Table 4). The ECD.CR generally had the lowest PM emission rate for all cycles tested, except for the NYB cycle, where the PM emission rate was similar to the rate from CNG vehicles. For all vehicles, the SS operation generated lower emission rates than transient operation.

Table 4. Vehicle mass particle emissions for each test cycle.

Vehicle Configuration	CNG.1	Diesel OEM	Diesel with CRT	CNG.2
Test Cycle	Ave PM Emissions \pm SD (mg/mile)			
CBD	39.9 \pm 12.5	119 \pm 6.97	14.1 \pm 0.35	33.4 \pm 1.2
SS	22.9 \pm 1.98	23.3 \pm 6.22	3.43 \pm 0.59	NT ^a
NYB	92.05 \pm 19.73	631 ^b	95.9 \pm 21.6	102 \pm 21.1
UDDS	23.1 \pm 2.81	90.6 \pm 5.43	16.6 \pm 1.96	23.7 \pm 2.85

^a Not Tested

^b Single composited sample of 3x NYBs

VOCs – 1,3-Butadiene, BTEX, and NMHC Emissions

Only the CNG vehicle emissions contained quantifiable concentrations of 1,3-butadiene as summarized in Table 5. These emissions are also driving cycle dependent according to the trends: NYB > CBD UDDS > SS. The 1,3-Butadiene emission rates for CNG.1 ranged from 2.0 to more than 11 mg/mi, while those for CNG.2 vehicle ranged from 0.9 to 2.8 mg/mi. Benzene emission rates

ranged from 0.06 mg/mi for ECD.CR to as high as 9.0 mg/mi for CNG.1 as shown in Table 5. For each vehicle configuration, benzene emissions were generally driving cycle dependent: NYB > CBD > UDDS > SS. A complete set of NMHC, BTEX, 1,3-butadiene, and styrene mass emission measurements are detailed in Table 5. The NMHC emission rates were not corrected for tunnel background effects. When multiple tests of the same cycle were run for a particular configuration, multiple values have been averaged and a corresponding standard deviation is provided.

Table 5. VOC emissions for each test cycle.

Compound	CBD				(mg/mi)	UDDS			
	CNG.1	ECD.OC	ECD.CR	CNG.2		CNG.1	ECD.OC	ECD.CR	CNG.2
1,3-Butadiene	3.4 ± 1.0	n.d.	n.d.	1.1		3.4	n.d.	n.d.	0.90
Benzene	3.2 ± 0.3	2.6 ± 0.5	0.59 ± 0.02	4.3		2.4	1.7 ± 0.2	0.29 ^c	3.3
Toluene	1.3 ± 0.3	0.31 ± 0.12	n.d.	3.0		0.63	0.38 ± 0.05	0.56 ^c	2.9
Ethylbenzene	n.d.	n.d.	n.d.	n.d.		n.d.	0.51 ^c	n.d.	0.17
m & p-Xylenes	0.13 ± 0.11	0.74 ± 0.01	n.d.	0.86		0.16	1.9 ± .02	n.d.	n.d.
o-Xylene	n.d.	n.d.	0.55 ^c	n.d.		0.02	0.57 ± 0.09	n.d.	0.92
Styrene	n.d.	n.d.	n.d.	n.d.		n.d.	n.d.	n.d.	n.d.
Total NMHC	1174 ± 104	70 ± 3	36 ± 4	2610		855	66 ± 5	23 ± 5	1117
Compound	NYB				(mg/mi)	SS			
	CNG.1	ECD.OC	ECD.CR	CNG.2		CNG.1	ECD.OC	ECD.CR	CNG.2
1,3-Butadiene	11	n.d.	n.d.	2.8		2.0	n.d.	n.d.	n.t.
Benzene	9	7.5	0.06 ^c	7.3		1.9	0.27 ± 0.05	0.12 ± 0.01	n.t.
Toluene	4.6	0.84	n.d.	n.d.		0.59	n.d.	0.04 ± 0.03	n.t.
Ethylbenzene	2.1	n.d.	n.d.	n.d.		n.d.	0.01 ^c	n.d.	n.t.
m & p-Xylenes	0.12	6.2	n.d.	n.d.		n.d.	0.10 ± 0.07	0.13 ± 0.01	n.t.
o-Xylene	n.d.	2.1	n.d.	n.d.		n.d.	0.01 ^c	n.d.	n.t.
Styrene	n.d.	n.d.	n.d.	n.d.		n.d.	n.d.	n.d.	n.t.
Total NMHC ^b	3282	381	34	4058		514	43 ± 19	9 ± 2	

^a Estimated as the sum of the quantifiable peaks measured from MR chromatogram.

^b Single run-no standard deviation. ^c No standard deviation due to measureable emissions in a single run.

n.d. = not detected; n.t. = not tested.

For all vehicle configurations, the BTEX emissions were dominated by benzene (Table 5). Toluene was observed in emissions from the CNG and EC.OC vehicles, but not from the ECD.CR vehicle. For the CBD and NYB cycles, toluene emissions from both CNG tests were greater than for the ECD.OC vehicle. Xylene emissions were higher for ECD.OC relative to CNG. For all driving cycles, the

estimated total NMHC emissions followed the trend: CNG.2 > CNG.1 > ECD.OC > ECD.CR. Total gas-phase HC emissions were cycle dependent as follows: NYB > CBD > UDDS > SS.

There were no significant tunnel background emissions of 1,3-butadiene, benzene, o-xylene, or total NMHC (Supplemental, Table A). Small amounts of m- and p-xylenes were observed in tunnel backgrounds after CBD testing of the ECD.CR and CNG configurations. Significant tunnel background emissions of toluene, ethylbenzene, xylenes, and styrene were observed for CNG.1 after the UDDS and NYB cycle tests that in some instances exceeded the measurements of test cycle emissions with the engine running. As the emissions from cleaner technologies decrease, the challenge is to provide measurements that can be distinguished over the tunnel background level and minimize variability of sampling. Many of the uncertainties of the measured emissions shown in Table 5 are of similar magnitude. This is a reflection of the increasing challenge to measure emissions from cleaner engine alternatives and new ways of sampling need to be considered.

VOC - Carbonyl Emissions

The emission rates for carbonyl compounds are summarized in Table 6 for the CBD and SS cycles in the samples and are uncorrected for tunnel background (Supplemental, Table B). The emissions from the CNG bus (CNG.1 or CNG.2) are much greater than from either of the ECD-fueled vehicles. The carbonyl emissions from CNG vehicles are primarily formaldehyde, with a total output approaching 1 g/mi for the CBD cycle. For ECD-fueled vehicles, formaldehyde was a smaller percentage of the total carbonyl emissions. All of the CNG and ECD-fueled buses emitted acetaldehyde.

The carbonyl emissions from the CNG and ECD-fueled vehicles over the SS driving cycle were generally lower than for the CBD cycle (Table 6). For the CNG.1 vehicle following the SS driving cycle, the highest carbonyl emission was formaldehyde (78 mg/mi). However, the total carbonyl emissions for the CNG.1 were almost 28% higher than those from the ECD.CR bus. Also, significant

emissions of higher molecular weight carbonyls, including valeraldehyde and hexanal, were observed for the ECD.CR vehicle.

Tunnel background samples for most all vehicle configurations had measurable levels of formaldehyde, acetaldehyde, acetone, propionaldehyde, and methyl ethyl ketone. Total carbonyl emissions from the tunnel background exceeded the levels measured for the ECD.OC bus (SS driving cycle) and for the ECD.CR bus (CBD driving cycle). Acetaldehyde was the predominant carbonyl species in all tunnel background emission samples, except for the ECD.CR in the SS driving cycle.

Table 6. Carbonyl emissions for CBD and SS test cycles.

Compound	CBD (mg/mi)				SS		
	CNG.1	ECD.OC ^a	ECD.CR ^b	CNG.2 ^c	CNG.1	ECD.OC ^a	ECD.CR ^b
Formaldehyde	773 ± 256	21 ± 7	3.9	713	78	1.0 ± 1.4	12
Acetaldehyde	83 ± 44	41 ± 50	3	70	n.d.	0.15 ± 0.22	2.7
Acrolein	4.2 ± 0.9	1.4 ± 9	n.d.	7.2	0.07	n.d.	0.75
Acetone	15 ± 13	20 ± 9	n.d.	7.5	n.d.	1.5 ± 2.1	3.4
Propionaldehyde	11 ± 5	1.4 ± 1.9	n.d.	1.7	n.d.	0.11 ± 0.15	10
Butyraldehyde	5.1 ± 2.6	1.6 ± 0.5	3.9	0.37	0.04	0.16 ± 0.07	2.3
Methyl Ethyl Ketone	0.8 ± 1.0	n.d.	0.25	0.05	n.d.	0.09 ± 0.13	n.d.
Methacrolein	1.6 ± 0.6	n.d.	0.91	n.d.	n.d.	0.04 ± 0.06	1
Benzaldehyde	1.4 ± 1.5	n.d.	n.d.	n.d.	0.27	0.09 ± 0.13	1.3
Crotonaldehyde	3.2 ± 1.3	n.d.	2	n.d.	0.1	0.08 ± 0.12	2.8
Valeraldehyde	0.8 ± 0.5	0.12 ± 0.17	n.d.	n.d.	n.d.	0.11 ± 0.15	11
m-Tolualdehyde	0.2 ± 0.5	21 ± 7	n.d.	n.d.	n.d.	0.06 ± 0.08	2.9
Hexanal	1.0 ± 0.9	0.53 ± 0.75	0.9	1.1	n.d.	0.08 ± 0.08	11
Total Carbonyl	900 ± 311	87 ± 69	15	801	78	3.5 ± 4.5	61

^a Diesel baseline carbonyl results have been designated as lower limits of emission rates (see text)

^b No standard deviation available because only one test had measureable emissions.

^c No standard deviation available since there was a single run performed for CNG.2. n.d. = not detected.

PAH Emissions

The emission rate for individual PAHs measured from filters and PUF are summarized in Tables 7 and 8, respectively. In general, for all vehicle configurations, PAH emission rates were highest for the NYB cycle and lowest for the SS test cycle. The ECD.OC had the highest total PAH emission rate for all test cycles. For example, the emissions of benzo(a)pyrene (BaP) from CNG.1 and CNG.2 vehicles over the NYB cycle were 0.75 and 0.41 µg/mi, respectively, but could not be detected in the

SS cycle. The BaP emission rates for ECD.OC were the highest for all vehicle configurations and test cycles at 0.31, 0.49, and 1.4 µg/mi for the UDD, CBD, and NYB cycles, respectively. BaP emissions for all other configurations reported levels that were near the detection limit or not detected (Table 7). Benz(a)anthracene and chrysene/triphenylene were reported or detected in all test configurations and drive cycles except the ECD.CR tested in the SS mode. For the ECD.CR, CNG.1, and CNG.2, PAHs with a molecular weight greater than 228 were either reported at levels close to the detection limit or not detected.

Semi-volatile phenanthrene emission rates for the NYB cycle for the CNG.1, ECD.OC, ECD.CR, and CNG.2 were 44, 67, 61, and 44 µg/mi, respectively. For the CBD test cycle, the same vehicle configurations emitted 17, 9.5, 8.6, and 22 µg/mi, respectively (Table 8). For the semi-volatile

Table 7. Particle-associated PAHs for each test cycle.

Vehicle Configuration	(u g/mi)															
	CNG.1				ECD.OC				ECD.CR				CNG.2			
	SS	UDDS	CBD	NYB	SS	UDDS	CBD	NYB	SS	UDDS	CBD	NYB	UDDS	CBD	NYB	
Test Cycle																
Naphthalene	0.12	0.13	0.65	1.6	ND	1.2	0.70	16	0.30	0.11	0.14	1.0	0.14	0.22	2.0	
2-methylnaphthalene	0.14	0.29	0.57	1.3	0.10	1.4	1.8	16	0.10	0.16	0.23	1.1	0.17	ND	ND	
1-methylnaphthalene	ND	ND	0.28	0.66	ND	ND	1.8	4.8	ND	ND	0.17	0.58	0.06	NQ	ND	
Biphenyl	ND	ND	0.21	0.40	0.10	0.71	0.60	8.7	ND	ND	0.17	0.041	0.042	NQ	0.68	
2,6-dimethylnaphthalene ^a	ND	0.09	ND	0.36	0.10	0.68	0.84	6.3	ND	0.040	0.054	ND	ND	ND	ND	
Acenaphthylene	ND	0.10	ND	0.68	ND	ND	0.75	2.0	ND	ND	ND	ND	ND	ND	2.2	
Acenaphthene	ND	ND	0.36	ND	0.50	ND	ND	ND	ND	ND	ND	ND	ND	ND	2.2	
2,3,5-trimethylnaphthalene ^b	0.09	0.18	ND	1.2	ND	ND	ND	ND	ND	ND	ND	0.54	ND	ND	D	
Fluorene	0.19	0.31	0.63	1.1	0.50	0.32	0.97	6.3	ND	0.22	1.1	0.51	0.085	ND	ND	
Phenanthrene	0.074	0.17	0.68	1.5	0.40	7.5	9.7	80	0.20	0.15	0.19	1.3	0.085	0.14	1.6	
Anthracene	ND	ND	ND	ND	ND	0.34	0.75	5.0	ND	ND	ND	ND	ND	0.044	ND	
1-methylphenanthrene	0.16	0.61	1.09	1.0	0.50	6.1	4.6	27	0.10	0.055	0.20	1.2	0.041	0.09	0.65	
Fluoranthene	0.13	0.26	0.94	1.9	1.50	6.5	6.5	39	0.20	0.26	0.27	1.5	0.14	0.22	2.0	
Pyrene	0.33	0.49	1.65	3.1	6.3	13	12	93	0.50	0.68	0.56	3.5	0.37	0.55	4.9	
Benz(a)anthracene	0.06	0.15	0.28	D	0.10	0.26	0.27	1.1	ND	0.029	0.034	0.20	0.051	0.11	0.62	
Chrysene/triphenylene	0.19	0.20	0.53	0.94	0.30	0.39	0.36	2.1	ND	0.11	0.053	0.31	0.24	0.28	1.9	
Benzo(b)fluoranthene	ND	ND	ND	ND	ND	2.5 ^c	0.42	3.0 ^c	ND	ND	ND	ND	0.066	ND	0.7	
Benzo(k)fluoranthene	ND	ND	ND	ND	ND	c	0.20	c	ND	ND	ND	ND	0.029	ND	ND	
Benzo(e)pyrene	ND	0.05	ND	ND	D	0.32	0.44	1.7	ND	ND	ND	ND	0.043	0.047	0.36	
Benzo(a)pyrene	ND	0.012	ND	0.75	D	0.31	0.49	1.4	ND	ND	ND	ND	ND	D	0.41	
Perylene	ND	ND	ND	0.95	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	
Indeno(1,2,3-cd)pyrene	0.06	ND	ND	D	ND	0.36	0.54	1.5	ND	ND	ND	ND	0.032	ND	0.5	
Dibenzo(a,h)anthracene	ND	0.11	ND	ND	ND	ND	0.35	1.3	ND	ND	ND	ND	ND	ND	ND	
Benzo(g,h,i)perylene	0.045	0.077	0.105	0.81	0.10	0.57	0.74	3.2	ND	0.019	ND	ND	0.034	D	0.47	
Total	1.58	3.21	7.97	18.2	10.5	40.9	45.2	317.2	1.40	1.83	3.15	11.9	1.64	3.15	21.2	

^a Co-elution with C2 naphthalene.

^b Co-elution with C3 naphthalene.

^c Benzo(b,j,k)fluoranthene co-elution

ND = not detected.

D = detected.

SS for CNG.2 not tested.

PAHs such as acenaphthene, emissions were higher for the CBD cycle than for the UDDS cycle except for EC.OC (Table 8). Of the alkyl PAHs, the emission rate of 2-methyl naphthalene was the highest for all vehicle configurations and drive cycles tested with the highest emission rate of 515 ug/mi for the ECD.OC tested on the NYB cycle. The emission rate for volatile PAHs trapped in the XAD are summarized in Table C, Supplemental and the XAD is corrected for PAH contaminant level in the XAD.

The levels of volatile and semi-volatile PAH's in the tunnel background were typically lower than samples. Generally, depending on the test cycle and the specific volatile PAH, the average background for ECD.CR samples, for example, were less than 30% of the sample. These levels however, we feel can contribute a significant portion to samples and therefore background corrections are not provided, but actual tunnel backgrounds are reported.

Table 8. Semi-volatile PAHs for each test cycle.

Vehicle Configuration	(µg/mi)														
	CNG.1				ECD.OC				ECD.CR				CNG.2		
Test Cycle	SS	UDDS	CBD	NYB	SS	UDDS	CBD	NYB	SS	UDDS	CBD	NYB	UDDS	CBD	NYB
Naphthalene	0.34	3.9	31	87	4.0	32	43	103	1.9	1.9	9.1	33	2.8	6.7	31
2-methylnaphthalene	0.38	5.6	40	110	5.7	110	70	129	3.7	2.0	15	62	3.1	5.1	28
1-methylnaphthalene	0.25	4.0	25	70	2.8	57	31	62	1.9	0.83	7.6	29	2.4	3.4	19
Biphenyl	ND	1.9	9.3	45	3.1	75	42	150	3.0	3.5	5.8	36	1.6	2.0	13
2,6-dimethylnaphthalene ^a	0.11	2.8	14	46	3.6	55	23	89	4.2	1.2	8.7	48	1.5	2.3	14
Acenaphthylene	0.12	4.6	12	33	1.0	ND	25	37	2.1	0.4	4.3	25	5.2	5.7	37
Acenaphthene	0.044	1.1	3.7	21	ND	11	5.7	ND	2.0	ND	5.9	30	0.75	1.4	9.0
2,3,5-trimethylnaphthalene ^b	0.26	5.6	8.2	28	3.4	8.6	7.6	24	3.1	2.0	8.3	54	2.1	4.3	17
Fluorene	1.8	4.4	7.1	26	1.8	ND	4.3	ND	1.6	3.2	4.7	28	3.1	6.2	18
Phenanthrene	3.3	9.4	17	44	22	9.6	9.5	67	3.9	8.1	8.6	61	9.9	21.9	44
Anthracene	0.64	1.3	2.4	7.4	ND	ND	ND	ND	ND	ND	ND	ND	1.4	3.0	6.4
1-methylphenanthrene	0.82	1.8	4.0	7.6	8.0	1.8	1.7	18	0.60	2.0	2.4	8.3	1.7	7.0	9.1
Fluoranthene	0.99	1.8	4.3	9.6	2.2	0.79	0.81	5.9	0.70	2.8	1.6	7.0	1.7	4.5	9.4
Pyrene	2.6	3.8	8.0	18	3.5	0.89	0.83	7.4	1.4	6.7	3.1	16	3.3	9.2	19
Benz(a)anthracene	ND	ND	0.31	ND	ND	0.20	ND	D	ND	ND	ND	ND	ND	ND	ND
Chrysene/triphenylene	ND	ND	0.45	ND	ND	0.20	ND	D	ND	ND	ND	ND	ND	D	ND
Total	11.6	52.0	187.5	552.3	61.0	362.8	264.9	694.1	30.1	34.6	85.5	437.3	40.7	82.7	273.7

^a Co-elution with C2 naphthalene.

^b Co-elution with C3 naphthalene.

ND = not detected.

D = detected.

Bioassay

Specific Mutagenic Activity

Specific mutagenic activity (SMA) refers to the number of revertant bacteria per mass of PM collected (rev/ μ g PM) as summarized in Table 9 for each tester strain with and without the addition of metabolic enzymes (S9). For tester strain TA98 and for all test cycles, the CNG vehicles had the highest SMA. For example, for the CBD test cycle for CNG.1, SMAs with and without S9 were 19 and 40 rev/ μ g PM, respectively (Table 9) which indicates that the most active compounds did not require the addition of metabolic enzymes. The SS and the UDDS test cycles had the highest SMAs with or without S9 (40 and 80 rev/ μ g with and without S9 for SS cycle, respectively) again indicating that the compounds responsible for the activity did not require the addition of metabolic enzymes. In general, the SMA of vehicle emissions tested in TA98 without S9 was consistently higher than with S9 added, independent of the test cycle. Dilution tunnel background samples had lower SMAs than samples from the vehicles tested and were typically less than 1.0 rev/ μ g for all cycles tested. An example of the low background tunnel contribution to the SMA of CNG.2 and ECD.CR emissions is presented in Figure 1. These results were typical for all the background tunnel samples tested.

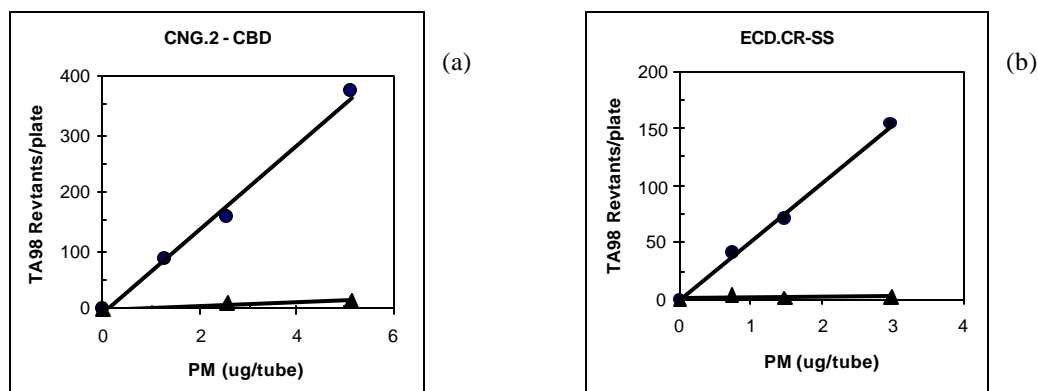


Figure 1. Dose response curves for CNG and ECD.CR samples tested in TA98 without metabolic enzymes added. (a) CNG.2 CBD sample(●) and matching tunnel background (▲). Composite of four CBD cycles. (b) ECD.CR Steady State driving cycle sample (●) and matching tunnel background (▲). Composite of 4 CBD equivalent times.

Several samples were also tested with strain TA98 NR in parallel with TA98 (-S9). The TA98 NR is insensitive to specific types of NPAHs. The NPAHs are highly potent mutagens and a decreased response with this tester strain compared to its immediate parent type (TA98, without S9) indicates the presence of certain NPAHs (20). The SMAs for all vehicle emissions over the CBD cycle tested for all vehicle configurations tested with TA98 (-S9) and in TA98 NR (-S9) are illustrated in Figure 2. In both CNG samples, the response in TA98 NR decreased, indicating that the CNG emission sample may contain NPAHs. There was little activity detected in ECD.OC and ECD.CR emission samples when tested in both TA98 and TA98 NR.

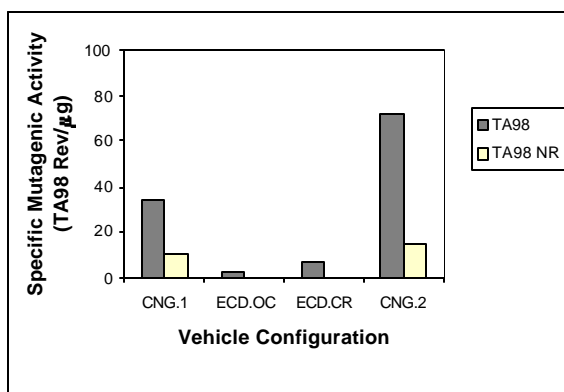


Figure 2. Specific mutagenic activity of vehicle configurations for the CBD cycle. (-S9) in tester strain TA98 NR. CNG.1 and ECD represents composite of 2 CBD cycles each; CRT and CNG.2 represent composite of 4 CBD cycles. The ECD and CRT samples did not have TA98 NR activity.

Table 9. Specific mutagenic activity (potency) for each test cycle.

Vehicle Configuration	CNG.1		ECD.OC		ECD.CR		CNG.2	
Metabolic enzymes	(+S9)	(-S9)	(+S9)	(-S9)	(+S9)	(-S9)	(+S9)	(-S9)
Test Cycles and Tester Strain	(Rev/μg)							
CBD								
TA 98	19	40	1.3	2.9	2.8	6.7	34	60
TA 100	12	4.5	1.6	1.2	0	0	12	11
UDDS								
TA 98	43	79	0.6	0.4	6.9	8.8	31	66
TA 100	16	6.2	0.0	1.4	6.8	2.5	10	5.7
NYB ^a								
TA 98	26	46	1.0	2.3	3.5	11	12	31
TA 100	4.2	16	2.6	1.6	0.0	0.0	5.6	13
SS								
TA 98	40	80	6.6	11	25	51	NT	NT
TA 100	12	10	4.4	2.5	9.6	7.3	NT	NT

^a Single composited sample of 3 NYB test cycles
NT =Not Tested

The SMAs of the emission samples tested in TA100 were generally lower than those tested in TA98, as summarized in Table 9. Most of the test cycles emissions except NYB had higher specific activity with S9 relative to activity without S9. The CNG.1 vehicle had the highest SMA for TA100 (S9) over the NYB test cycle (16 rev/ μ g).

Mutagenic Emissions

The mutagenic emissions (ME) present in the PM and vapor-phases as tested in TA98 are summarized for all test cycles in Figure 3 (TA98 Rev/mi $\times 10^5$). The ME rate incorporates the SMAs of the sample and the total sample volume. In general, the highest ME was observed without the addition of S9. For TA98, the highest ME is observed in the NYB test cycle, followed by the CBD, UDDS, and SS test cycles. The CNG vehicles had the highest ME of all test vehicles. The contribution of the VP to the ME rate was lower than for PM and was test cycle dependent. For example, VP

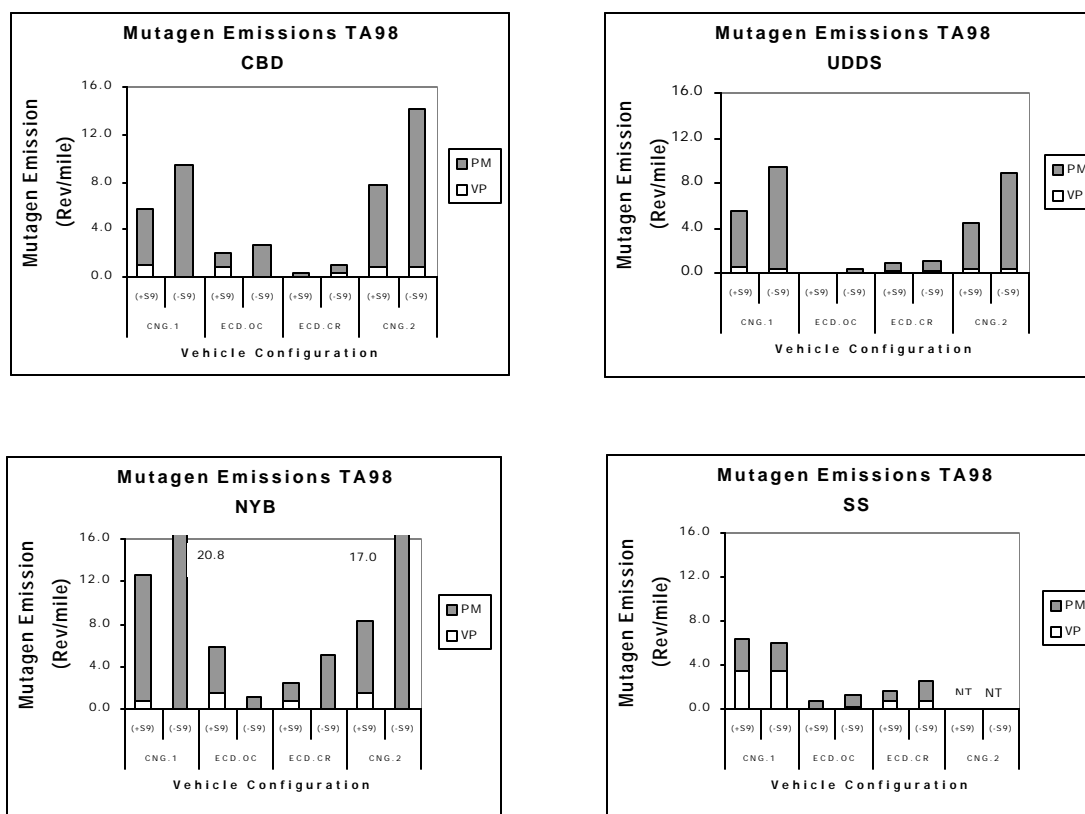


Figure 3. Mutagen emission rates for vehicles and different test cycles. TA98 with (+S9) and without (-S9) metabolic activation for both the particle (PM) and vapor (VP) phases. NT= not tested.

emissions from the CNG vehicle during the CBD test cycle were up to 6% of PM ME when tested in TA98 without S9. When tested with S9, VP emissions from the CNG.1 vehicle contributed approximately 18% of the total ME for the CBD test cycle (Fig. 3). For the CNG.1 vehicle over the SS test cycle, VP emissions accounted for approximately 50 to 60% of the total ME, with and without S9 added, respectively.

The ECD.OC and ECD.CR vehicles had lower ME rates than the CNG vehicle for all test cycles. For example, for testing using tester strain TA98, and tested in the CBD test cycle, the total ME for ECD.OC averaged approximately 30% and 24% of the CNG.1 total ME, with and without S9, respectively. The ECD.CR configuration averaged approximately 4% and 9% of the total ME for the CNG.1 vehicle with and without S9, respectively.

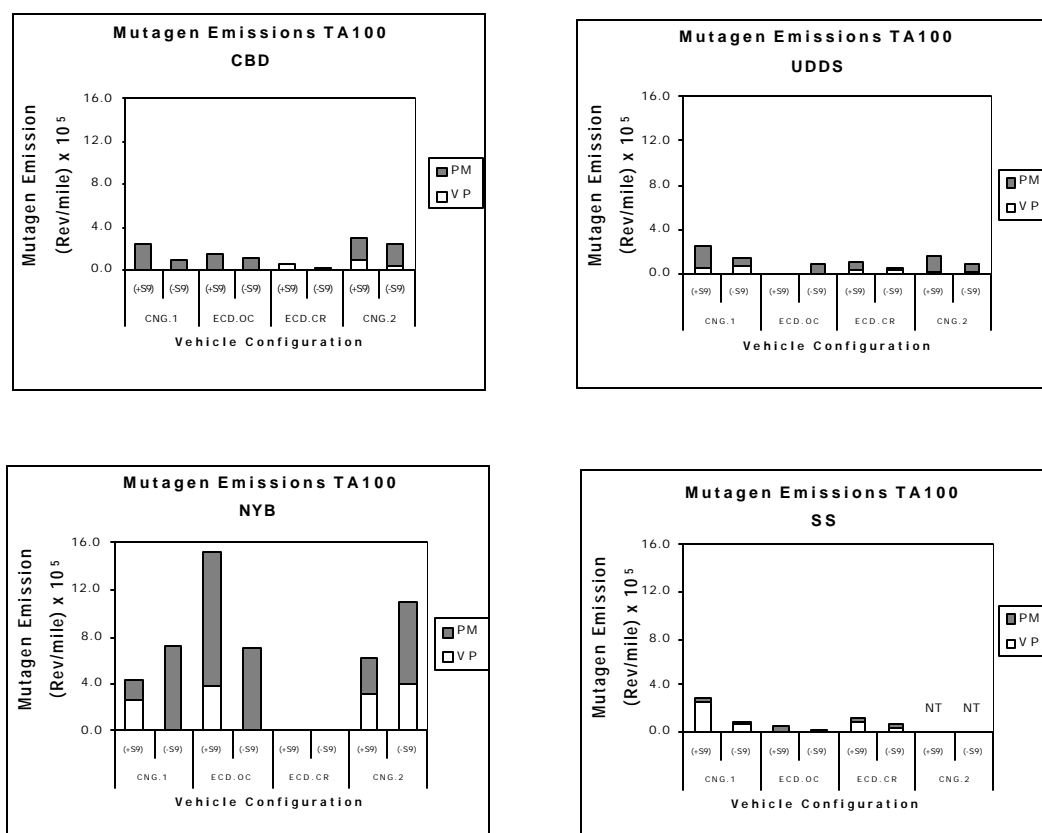


Figure 4. Mutagen emission rates for vehicles and different test cycles. TA100 with (+S9) and without (-S9) me activation for both the particle (PM) and vapor (VP) phases. There was no dose response detected in the ECD.OC sample tested at 0.7 $\mu\text{g}/\text{tube}$ to 2.4 $\mu\text{g}/\text{tube}$ (see Table 9) and therefore the emissions were determined to be zero under the conditions of the test program NT=not tested.

The total ME rates for vehicles tested in strain TA100 are also summarized in Figure 4. Overall, the total ME rate in TA100 is lower than in TA98 for all test cycles and was typically less than 2×10^5 rev/mi. Also, the contribution of VP to total ME was similar to that observed in TA98. However, there are some distinct differences observed with TA100 for the CBD, UDDS, and SS test cycles. First, the SMA with S9 is higher than without S9 for all vehicle configurations. Second, the CNG.1 vehicle had the highest ME rates for the NYB test cycle without S9, but the ECD.OC had the highest ME with S9. Third, the VP phase for CNG.1 and ECD.OC vehicles over the NYB cycle had ME, but the ECD.CR did not have ME with or without S9. Fourth, the SS cycle for TA100 had higher VP ME compared to PM. Finally, with the exception of the NYB cycle, the CNG.1 had a ME rate that was similar to the ECD.OC or ECD.CR, especially with S9.

DISCUSSION

The PM measurements were consistent between test runs for the same vehicle configuration, especially for the transient test cycles. Although the CNG.1 and CNG.2 tests were conducted a few months apart, the PM emission rate serves as one indicator of a reproducible sample from this in-use vehicle. However, it is noted that a new oxygen sensor was installed in the vehicle and the software was upgraded prior to the CNG.2 tests as part of routine in-use maintenance. The impact of this maintenance event was not assessed. As expected, the PM emissions for the transient cycles were highest for the baseline ECD.OC and lowest for the ECD.CR. Additional discussion related to the total PM emissions was presented previously (11).

The levels of tunnel background are an issue recognized by the mobile emissions test community, but in most cases has not been addressed. We were one of the initial research teams to illustrate this problem, especially with cleaner engine technologies. Since the dilution tunnel system itself becomes a source for relatively low levels of some toxic contaminants, we initiated extensive tunnel conditioning prior to sample acquisition. However, despite these quality assurance measures,

some toxic contaminants remain as part of the tunnel coating and as illustrated in the tunnel background levels of some VOCs as presented in the Supplemental Tables. To decrease the background levels as much as practical, we routinely condition the tunnel before sampling as indicated. First, approximately 1×10^5 cubic feet of dilution air is passed through the tunnel. This is followed by hot exhaust at steady state for 35 min. We felt it important to report the background levels directly rather than subtracting it from the sample. Again these levels become important as the newer engine and control technologies become available, and we feel therefore that new approaches for sampling will need to be considered for the future to meet the lower emission rates.

VOCs

The results of VOC analysis indicate that the CNG bus without exhaust control technology had comparable or higher emissions of toxic hydrocarbons than a diesel bus equipped with either an oxidation catalyst or a particulate filter. Of particular concern are the emissions of 1,3-Butadiene, which is a potent animal carcinogen (22). Only the CNG-fueled buses emitted measurable levels of this compound. Emissions were observed in all of the test cycles, varying from 0.9 to 11 mg/mile. These butadiene emission levels are comparable to those observed in a fleet of high mileage, light-duty, gasoline-powered vehicles tested on the FTP cycle (23). The emissions of BTEX from ECD.OC and CNG vehicles are approximately an order of magnitude lower than emissions observed in the same fleet of 35 gasoline-powered vehicles (23). For example, the average benzene emissions alone for the in-use light-duty gasoline vehicles tested was 28 mg/mi. The BTEX emissions are significantly reduced on trap-equipped diesel vehicles when compared to either CNG vehicles or diesel vehicles with an oxidation catalyst.

The differences between CNG and diesel vehicles are considerably more pronounced for emissions of carbonyl compounds. For the CBD cycle, the diesel buses emitted between 15 and 100 mg/mi of total carbonyls, but the carbonyl emissions from the CNG buses are roughly an order of magnitude greater. For formaldehyde, CBD cycle emission rates for the diesel buses were at or below

the California emissions standard of 15 mg/mile for light duty gasoline vehicles (measured using the FTP cycle). CNG bus emissions were over 50 times higher than the light duty vehicle standard. Inferences regarding the emissions of acetaldehyde and several other carbonyl compounds are difficult to make because of the high tunnel background emissions which sometimes approached or exceeded sample concentrations. Tunnel background concentrations are presented in Supplemental Tables A and B available on the web version of this paper. Future testing will have to address the issue of adsorption and carryover of compounds in the dilution tunnel. It should also be noted that the sum of the 13 target carbonyl compounds may not accurately represent the total carbonyl emission rate. This is probably not significant for the CNG vehicle where most of the carbonyls come from the lowest molecular weight compounds. However, for diesel vehicles, these target compounds represent a smaller fraction of the total carbonyl compounds emitted.

PAHs

The current study is one of the first reports on PAH emissions from CNG-fueled heavy-duty vehicles over multiple driving cycles. One finding is PM emission reductions for the trap-equipped bus as compared to the non-trap equipped bus do not necessarily indicate a similar decrease in all PAHs. For the NYB cycle, ECD.CR PM emissions were 85% lower than ECD.OC, whereas volatile PAHs such as 1-methyl naphthalene and 2-methyl naphthalene were reduced by only 43% and 54% respectively. On the other hand, benz(a)anthracene and chrysene emission reductions of 81% and 85% respectively, were similar to the PM emissions reduction.

One observation also previously reported by Lev-On (9) and Grägg (6) is the emissions of volatile and semi-volatile PAHs from CNG-fueled vehicles. Of particular interest is the reported emission of alkyl PAHs such as alkyl naphthalenes and methyl phenanthrenes which are attributed mainly to uncombusted diesel fuel. Since CNG fuel is primarily methane and contains trace levels of compounds with more than six carbons, it is highly unlikely that the main source of alkyl-PAH

emissions from CNG is uncombusted fuel. PAH emissions may be attributed to products of combustion or other sources such as the lubricating oil.

One finding from this study is that tunnel background levels can contribute significantly to some of the emission samples. Most dilution tunnels have a background level of exhaust components because these components are absorbed to walls when exhaust is passed through the tunnel and are desorbed randomly off the wall in subsequent tests. Also, the tunnel background contribution may vary depending on many factors including the vehicle technology tested. For example, desorption from the tunnel wall during a CNG test may be higher than an ECD.OC test due to the higher temperature of the CNG exhaust. Because the tunnel background contribution is not well understood, the data are presented uncorrected for tunnel background contributions. Finally, as engine emissions decrease, the relative contribution of the tunnel background will increase.

When comparing the PAH emission profile from the ECD.CR and OEM using low sulfur diesel fuel, there appears to be a relative decrease in PAHs with molecular weights greater than 228. Westerholm et al (4) reported similar results for European low sulfur diesel fuel (MK1) tested in a diesel engine not equipped with a particle filter or trap. Lanni et al. (24) reported results from a study comparing PAH emissions from a diesel bus tested with or without a CRTTM device using the NYB cycle. In their study, emissions of semi-volatile PAHs were generally lower than in our study, possibly due to differences in fuel composition or analyses. Lev-On et al. (9) also reported decreases in PAH emissions with a CRTTM device.

Grägg (6) tested a CNG vehicle equipped with oxidation catalyst and detected PAHs that were predominantly in the semi-volatile phase. The highest emission rates were for fluoranthene (44 µg/mi) and pyrene (160 µg/mi). In comparison, emissions of these PAHs were lower in our study, independent of test cycle. Lev-On (9) tested two CNG vehicles on the CBD test cycle. One vehicle tested was the

same one used in this study. Volatile and semi-volatile PAH emissions from the transit bus tested in both studies were generally within a factor of two.

Bioassay

For the vehicle configurations tested with most of the driving cycles, the SMA's were higher for tester strain TA98 than TA100, a result that is different from previous observations with conventional diesel PM emission samples (13). The SMA's measured in the current study using TA98 without S9 were some of the highest observed for heavy-duty PM emissions using the Salmonella microsuspension assay and approached 70 rev/ μ g for UDDS and CBD cycles. In comparison, the PM from a 1993 Cummins L10 engine fueled by California Reformulated Diesel had approximately 19 rev/ μ g PM (TA98, +S9) and 26 rev/ μ g (TA98, -S9) (13).

The chemical species responsible for the mutagenic activity in the CNG bus samples are unknown, but the results for TA98 NR may indicate that there are NPAH compounds present in the sample. Further tests are required to chemically characterize the compound or class of compounds responsible for this activity. Although we used a common procedure for the extraction of diesel and ambient air PM-associated mutagenic compounds, the finding that the baseline ECD.OC diesel PM required toluene for the extraction of higher molecular weight PAHs indicates that it might be necessary to use other solvents to extract these mutagenic compounds. Since the PM from the ECD.OC vehicle is composed of elemental carbon, this may serve as a strong adsorbent for these compounds and may require other than the traditional methods of extraction to determine their effect on mutagenic activity.

The CNG vehicle emission samples tested with TA98 (-S9) had the highest SMA. However, there were marked differences between the emissions when tested in TA98 and TA100 which indicates that there may be different types of compounds responsible for the mutagenic activity. However, this requires further study and confirmation.

Westerholm et al (4) tested vehicle emissions in the standard Ames (19) assay and found that mutagenic activity was reduced 75 to 90% when using a MK1 fuel. They also reported that PM mutagenic activity was higher when tested without S9 and observed a higher emission rate with TA100 than with TA98. The emissions of semi-volatile phase were lower than those in the PM phase. Grägg (6) reported a 3-fold higher emission using TA100 (\pm S9) than for TA98 (\pm S9) from CNG-fueled buses equipped with an oxidation catalyst and reported a 3-fold higher emission using TA100 than for TA98 with or without metabolic enzymes added. In comparison, we found considerably higher SMA and ME using strain TA98. In the Grägg study (6), the semi-volatile phase had the highest emission rates overall, especially when tested using TA98 with S9. The reason for the difference between the two studies was not stated. However, differential sensitivities of the tester strains may indicate differences in sample composition, test and sampling conditions.

As stated previously, SMAs for the CNG vehicles tested were some of the highest that we have measured for emission sources and ambient samples. Although the mass of PM was lower than conventional diesel vehicles fueled by No. 2 diesel, the ME value is near what has been reported for vehicles using higher sulfur diesel fuel (50 ppm). A high SMA indicates that the PM, on a per mass basis, has a high potency. The source of the mutagenic activity remains unknown, but the combustion of lubricating oil may produce mutagenic compounds that contribute to the observed activity. The oil consumption rate during tests was not quantified in our study.

Based on a number of national and international organizations, short-term bioassays such as the Salmonella/microsome test are considered an important approach for evaluating the chemical nature of the emissions. The paper is not meant to provide a quantitative risk assessment for cancer. Rather, it is a comparative characterization of the emissions for toxic air pollutants, including the use of bioassay to help evaluate exposure evaluation and hazard identification for the complex mixture of emissions. The sensitivities and specificities of chemical compounds for this assay are well known and recognized.

Summary

The emissions from CNG- and ECD-fueled vehicles contain a complex mixture of toxic compounds, many of which are known or probable human carcinogens as seen in diesel exhaust (25). These types of compounds have been measured in ambient air, especially near or inside motor vehicles. Rodes et al. (26) reported in-vehicle and roadside PM and VOC concentrations while traveling selected California highways. The authors reported that pollutant exposures from vehicles immediately in front of the test vehicle were significant, accounting for 30 to 50% of the total in-vehicle commute exposures. Fitz et al (27) measured conventional diesel, diesel with trap, and CNG-powered school buses and reported that based on in-cabin measurements, higher exposures are occurring within the older buses than the newer trap-equipped and CNG-fueled buses. The in-cabin levels recorded are due to existing concentrations of pollutants on highways plus the infiltration of the buses' own emissions.

Relative to older buses or buses without after-treatment, the emissions from our test vehicles will likely compare favorably. However, our current focus on in-use configurations of "clean technology" transit buses is representative of current bus fleets. For example, most CNG transit buses in service in California as well as in national urban areas, indeed have no after-treatment since these buses (without after-treatment) meet the more stringent bus emission standard. Further, there are few diesels in bus fleets without oxidation catalyst. Our study primarily focused on toxic air pollutant emissions that should be quantitated to help evaluate public exposure. A companion paper addresses these technologies with after-treatment.

We present information on the comparative emissions of in-use transit buses using "clean technologies" Since the unit risk from the CNG exhaust would be difficult to calculate without epidemiological or chronic animal bioassay data, quantitative risk assessments for cancer are difficult to estimate. However, the emissions profiles for the toxic compounds and mutagenic activity measured, we feel provide information for future health assessments.

The lubricating oil consumption by the CNG engine is the likely contributor to the measured levels of PM in the emissions, as operationally defined by our collection and measurement techniques. We also feel that it is important for the public and scientific community, especially regarding public exposures, to be informed that CNG combustion (including oil consumption) and that diesel with oxidation catalyst produces emissions that includes toxic components including PAHs, BTEX, Carbonyls, and genotoxic activity. From a public exposure and health perspective, whatever the origin of the combustion source- fuel or oil, this would be important information to report.

With respect to PM, if the PM size from these types of buses are less than 1 μm or in the nano-particle size range, they are likely to be inhaled deep into the lung where PM-absorbed potent mutagenic compounds including PAHs could be delivered to target tissues or organs in the body. The emissions of toxic compounds from the vehicle types tested could be important for the risk evaluation of both acute and chronic human health effects (1, 25). Future work planned will include the study of advanced emission control technologies for diesel- and CNG-fueled vehicle applications. The effectiveness of oxidation catalyst control for the reduction of toxic emissions for CNG bus applications is of particular interest. Recently, a new transit “advanced technology” bus powered by a Cummins-Westport C Gas-Plus engine and OEM-equipped with an oxidation catalyst was recruited from fleet service and tested. Our group has reported preliminary findings (12). Results from this work are compared to the present study and presented in a companion publication (28).

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Supplemental Section

Supplemental Table A. Tunnel Background for VOCs (mg/mi).

Compound	CBD ^a				(mg/mi)	UDDS ^b			
	CNG.1	ECD.OC	ECD.CR	CNG.2		CNG.1	ECD.OC	ECD.CR	CNG.2
1,3-Butadiene	n.d.	n.d.	n.d.	n.d.		n.d.	n.d.	n.d.	n.d.
Benzene	0.01	n.d.	n.d.	0.58		n.d.	0.1	n.d.	n.d.
Toluene	n.d.	n.d.	n.d.	0.43		n.d.	0.19	n.d.	0.85
Ethylbenzene	n.d.	n.d.	n.d.	0.39		n.d.	n.d.	n.d.	0.10
m & p-Xylenes	0.57	n.d.	0.19	1.7		n.d.	n.d.	n.d.	0.47
o-Xylene	n.d.	n.d.	n.d.	n.d.		n.d.	n.d.	n.d.	n.d.
Styrene	n.d.	n.d.	n.d.	1.4		n.d.	n.d.	n.d.	0.47
Total NMHC	n.d.	n.d.	6.20	38		2.4	0.02	0.66	18

	NYB ^c					SS ^d			
	CNG.1	ECD.OC	ECD.CR	CNG.2		CNG.1	ECD.OC	ECD.CR	CNG.2
1,3-Butadiene	n.d.	n.d.	n.d.	n.d.		n.d.	n/a	n.d.	n.t.
Benzene	0.01	n.d.	n.d.	1.2		0.08	n/a	n.d.	n.t.
Toluene	0.02	n.d.	n.d.	4.5		0.59	n/a	n.d.	n.t.
Ethylbenzene	n.d.	n.d.	n.d.	0.78		n.d.	n/a	n.d.	n.t.
m & p-Xylenes	n.d.	n.d.	n.d.	0.65		n.d.	n/a	n.d.	n.t.
o-Xylene	n.d.	n.d.	n.d.	n.d.		n.d.	n/a	n.d.	n.t.
Styrene	n.d.	n.d.	n.d.	2.2		n.d.	n/a	n.d.	n.t.
Total NMHC	35	n.d.	n.d.	48.8		4.9	n/a	n.d.	n.t.

^a Mass emitted during test divided by 2.0 miles.

^b Mass emitted during test divided by 7.5 miles.

^c Mass emitted during test divided by 1.18 miles

^d Mass emitted during test divided by 8.7 miles.

n.d. = not detected; n/a = not available; n.t. = not tested.

Supplemental Table B. Tunnel Backgrounds for Carbonyls (mg/mi).

	CBD ^a				SS ^b		
	CNG.1	ECD.OC ^c	ECD.CR	CNG.2	CNG.1	ECD.OC ^c	ECD.CR
Formaldehyde	23	10	20	14	5.4	4.5	n.d.
Acetaldehyde	82	37	66	41	8.0	12	n.d.
Acrolein	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Acetone	20	7.8	18	12	3.2	1.5	n.d.
Propionaldehyde	3.0	0.11	2.0	1.4	0.23	0.13	n.d.
Butyraldehyde	2.2	0.13	n.d.	n.d.	0.41	n.d.	n.d.
Methyl Ethyl Ketone	0.04	n.d.	1.6	0.98	0.16	n.d.	0.03
Methacrolein	1.2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Benzaldehyde	1.6	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Crotonaldehyde	1.7	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Valeraldehyde	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.08
m-Tolualdehyde	n.d.	n.d.	n.d.	n.d.	0.07	n.d.	n.d.
Hexanal	2.4	n.d.	2.0	n.d.	n.d.	n.d.	n.d.
Total Carbonyl	137	55	110	69	18	18	0.11

^a Mass emitted during test divided by 2.0 miles. ^b Mass emitted during test divided by 8.7 miles. ^c Diesel baseline carbonyl results have been designated as lower limits of emission (see text). n.d. = not detected.

Supplemental Table C. Volatile PAHs in each test cycle.

Vehicle Configuration	CNG.1				ECD.OC				ECD.CR				CNG.2 ^a		
Test Cycle	SS	UDDS	CBD	NYB	SS	UDDS	CBD	NYB	SS	UDDS	CBD	NYB	UDDS	CBD	NYB
(ug/mile)															
Naphthalene	<50	<40	<350	NA	<50	<250	<350	980	75	81	200	930	110	130.0	480
2-methylnaphthalene	11	36	36	NA	6.2	120	55	370	11	39	34	230	34	40	130
1-methylnaphthalene	7.5	23	22	NA	3.1	53	24	240	5.5	17	17	110	23	27	80
Biphenyl	ND	ND	5.7	NA	0.90	2.7	4.3	55	1.1	ND	3.1	27	2.7	ND	19
2,6-dimethylnaphthalene ^b	ND	ND	15	NA	1.6	4.3	12	62	1.7	ND	5.4	43	2.1	9.4	16
Acenaphthylene	ND	ND	2.9	NA	0.10	ND	ND	7.4	ND	ND	ND	ND	1.9	7.3	8.1

^a SS test cycle not available.

^b Co-elution with C2 naphthalene.

ND = not detected.

NA = Not available.

The XAD-4 resin is known to contain background levels of some PAHs that can interfere with the measurement of volatile PAHs (13). The XAD background was estimated by obtaining the average and standard deviation of the background level from six XAD. For the XAD results of naphthalene, 1- and 2- methyl naphthalene, biphenyl, 2,6-dimethyl naphthalene, and acenaphthylene only, the average background level was subtracted and corrected values falling below one standard deviation of the background were not reported. Levels of acenaphthene, and PAHs with molecular weights of 166 and greater measured in the XAD are not reported since they are thought to be attributed to XAD background levels rather than from actual vehicle emissions. This is supported by subsequent research conducted by this group that shows breakthrough of these PAHs from the filter or PUF would be unlikely.